

## DFT-based calculations of silicon complex structures in KF–KCl–K<sub>2</sub>SiF<sub>6</sub> and KF–KCl–K<sub>2</sub>SiF<sub>6</sub>–SiO<sub>2</sub> melts

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**Abstract:** The length and energy of bonds in the complex anions of silicon formed in KF–KCl–K<sub>2</sub>SiF<sub>6</sub> and KF–KCl–K<sub>2</sub>SiF<sub>6</sub>–SiO<sub>2</sub> melts were evaluated using the method of first-principles molecular dynamics, accomplished by means of the Siesta program. The effect of K<sup>+</sup> (from the second coordination sphere) on the stability of these complexes was studied. The bond lengths in the silicon complexes was found to change with increasing amount of the potassium ions. It was established that the following complexes [SiO<sub>4</sub>]<sup>4-</sup>, [SiO<sub>3</sub>F]<sup>3-</sup> and [SiF<sub>6</sub>]<sup>2-</sup> are the most stable in KF–KCl–K<sub>2</sub>SiF<sub>6</sub> and KF–KCl–K<sub>2</sub>SiF<sub>6</sub>–SiO<sub>2</sub> melts. The [SiO<sub>4</sub>]<sup>4-</sup> and [SiF<sub>6</sub>]<sup>2-</sup> complexes are thermally stable in the molten salt in the temperature range of 923–1073 K, whereas the [SiF<sub>7</sub>]<sup>3-</sup> structure, which is typical for the lattice of crystalline K<sub>3</sub>SiF<sub>7</sub>, is unstable in this temperature range. In the KF–KCl–K<sub>2</sub>SiF<sub>6</sub>–SiO<sub>2</sub> melts, conditions above 1043 K were created allowing the transformation of [SiO<sub>3</sub>F]<sup>3-</sup> into [SiO<sub>4</sub>]<sup>4-</sup>. Within the studied temperature mode, the Si–F bond length is in the range 1.5–1.9 Å and the Si–O bond lengths is 1.5–1.7 Å. The obtained results are in a good agreement with *in situ* data of Raman spectroscopy for the KF–KCl–K<sub>2</sub>SiF<sub>6</sub> and KF–KCl–K<sub>2</sub>SiF<sub>6</sub>–SiO<sub>2</sub> melts.

**Keywords:** molten salts; silicon complexes; structure; DFT calculations.

### INTRODUCTION

Nowadays, molten salts are used as electrolytes for a significant number of industrial electrochemical processes intended for metals production. Moreover, molten salts are of great importance for the development of nuclear energy<sup>1</sup> and the reprocessing of spent nuclear fuel.<sup>2</sup> They can be employed for the production of materials for chemical current sources and solar power.<sup>3</sup> An important direction of chemical research in the field of solvents based on molten salts is the study

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of the structure of groups of complexes. The physicochemical properties of molten salts, their morphological structure, and the chemical composition of electrode products largely depend on the composition, structure, and concentration of the complex groups.<sup>4</sup> Studying the electrode processes, especially in cases of the presence of a redox couple,<sup>5,6</sup> the interpretation of polarization data depends on the identification of the complex groups. The information regarding the structure of melts allows an understanding of the mechanisms of physicochemical processes during interaction of the substances with the molten salts. Knowledge of the structure and stability of the complexes is necessary in order to express the overall reactions in the electrochemical cell, as well as to determine the mechanisms of the electrode reactions.

Molten salts are aggressive media. Their use requires a careful selection of the construction materials. Molten salts containing compounds of metals can interact with the moisture and oxygen of ambient air. This interaction can lead to a change in the composition and structure of the complexes, and to alteration in the physicochemical properties of the molten media. An atmosphere of inert gases is required in order to use hygroscopic melts. The specific properties of the media necessitate the development of model approaches for their study. The experimental study of the structure of complex compounds is difficult and a not always solvable task in attempts to explain the processes occurring in molten salts.<sup>7–9</sup> There are a number of approaches providing an opportunity to consider the structure of complex groups and to explore the interaction processes of the substances in molten salts. The study of the melts structure can be performed on quenched melt samples.<sup>7</sup> Moreover, at room temperature, Raman data of solid samples may not take into account the destruction of individual components during the melting of the sample, as well as instability of the particles at high temperature. The study of the structure of melts,<sup>8,10</sup> including alkali halides,<sup>9</sup> can be realized *in situ* at high temperatures. A Raman spectroscopy study of molten salts gives a sufficiently clear idea regarding the structure of complexes. However, there are some limitations for applying this approach to halide molten salts. The concentrations of the complex groups should be significant for registration of vibrational bands with a high spectral peak. A substantial uncertainty may arise when studying melts with a low concentration of complexes. The evaporation of molten salts makes it difficult to record the scattered radiation. A condensation of the melt vapors on the cold parts of the experimental installation can cause damage to the equipment.

The DFT-based calculations can be applied for determining the structures of complex groups and evaluating interactions in melts.<sup>11</sup> This method is widely used for studying the structure and interaction in the low-temperature systems.<sup>12</sup> The DFT calculations were in a good agreement with results obtained for rapidly frozen samples of high-temperature silicate systems.<sup>3</sup> Based on the calculations,

it is possible to conceptualize the structure of molten salts.<sup>1</sup> An advantage of the simulation approach is a possibility of studying the structure and stability of complexes of molten alkali halides with complicated compositions in a certain temperature range. The data obtained by simulation can significantly complete the experimental results. Nevertheless, the conclusions of such calculations should be verified by experiment. Ionic melts of alkali halides based on KF–KCl containing  $\text{K}_2\text{SiF}_6$  and  $\text{SiO}_2$  are quite widespread in electrochemical processes for silicon production. They are well studied by the direct method (*in situ*) of the Raman spectroscopy. The high-temperature Raman spectra of KF–KCl– $\text{K}_2\text{SiF}_6$  and KF–KCl– $\text{K}_2\text{SiF}_6$ – $\text{SiO}_2$  melts were obtained in literature,<sup>9</sup> where the process of the silicon oxide dissolution was considered. It was established that complexes of the  $[\text{SiF}_6]^{2-}$  type are common for KF–KCl– $\text{K}_2\text{SiF}_6$  melts. The complexes  $[\text{SiO}_4]^{4-}$  and  $[\text{SiO}_3\text{F}]^{3-}$  were revealed to be formed in KF–KCl– $\text{K}_2\text{SiF}_6$ – $\text{SiO}_2$  melts. These data can be specified using DFT calculations. A comparison of the calculated data with the experiment<sup>9</sup> verifies the proposed model. The previous experimental studies<sup>9</sup> allowed the determination of the mechanism of  $\text{SiO}_2$  dissolution in KF–KCl– $\text{K}_2\text{SiF}_6$  melts. It is accompanied by the formation of isolated silicate tetrahedrons, silicon oxyfluoride groups, and gaseous silicon tetrafluoride. The thermal gravimetry method determined that the addition of  $\text{SiO}_2$  to a KF–KCl– $\text{K}_2\text{SiF}_6$  melt leads to increased mass loss at temperatures higher than the melting point of the mixture. The mass spectrometry method detected that the mass loss occurred due to  $\text{SiF}_4$  formation.

The purpose of this work was to investigate the structure of the complexes in KF–KCl– $\text{K}_2\text{SiF}_6$  and KF–KCl– $\text{K}_2\text{SiF}_6$ – $\text{SiO}_2$  molten systems applying DFT calculations and to reveal the effect of the temperature change on the stability of silicon complexes.

#### COMPUTATION AND MATERIALS

Molten salts possess ionic conductivity. The structural units of molten salts are ions, and the ionic complexes are in constant electrostatic interaction.

##### *Theoretical background*

The energy properties of the silicon complexes were investigated by performing the generalized gradient approximation (GGA) within the framework of the density functional theory.<sup>13</sup> The GGA was used to calculate the exchange-correlation potential, which in this case is represented as a function of density and its first derivative. The PBE functional developed based on the rational expansion function of the reduced gradient was used.<sup>14</sup> This functionality does not contain empirically optimized parameters and allows the accurate calculation of the energy characteristics of the investigated complexes.<sup>14,15</sup> The standard procedure for the decomposition of the orbitals in a basis was used. Plane waves were chosen as the basis.

##### *Materials*

In this work, the stability of the silicon complexes formed in KF–KCl– $\text{K}_2\text{SiF}_6$  and KF–KCl– $\text{K}_2\text{SiF}_6$ – $\text{SiO}_2$  melts, was studied using the quantum mechanics method, implemented in

the Siesta software package.<sup>12</sup> The calculations were performed for the silicon complexes: fluoride ( $\text{SiF}_x$ , where the integer  $x = 4-7$ ), oxyfluoride ( $\text{SiO}_3\text{F}$ ,  $\text{SiO}_2\text{F}_2$ ,  $\text{SiOF}_3$ ), and oxide  $\text{SiO}_x$  and  $\text{Si}_2\text{O}_y$  (where  $x = 2-4$ ;  $y = 4-7$ ). The effect of a whole number of potassium ions (from 1 to 3) on the structure of the complexes as part of the second coordination sphere was investigated.

The geometric optimization with the use of the generalized gradient approximation in the form of PBE was performed for all considered complexes. The dynamic relaxation of atoms was performed until the change in the total energy of the system was less than 0.001 eV. The energy of cutting the plane waves basis was assumed equal to 300 Ry.

The thermal stability of the silicon complexes was studied in a Nose–Hoover thermostat after geometric optimization. The silicon complexes were placed in the thermostat and sustained at temperatures of 923, 1023, 1043, and 1073 K during 2000 time steps (one step – 1 fs).

The bond energies in the silicon complexes were calculated using the equation:

$$E_{\text{bond}} = E_{\text{SiOF}} - N_{\text{Si}}E_{\text{MSi}}N_{\text{F}}E_{\text{F}} - N_{\text{O}}E_{\text{O}} \quad (1)$$

where  $E_{\text{SiOF}}$ ,  $E_{\text{Si}}$ ,  $E_{\text{F}}$  and  $E_{\text{O}}$  are the total energy of the complex, and the energies of a single silicon ion ( $\text{Si}^{4+}$ ), fluorine ( $\text{F}^-$ ) and oxygen ( $\text{O}^{2-}$ ), respectively, and  $N_{\text{Si}}$ ,  $N_{\text{F}}$  and  $N_{\text{O}}$  are the amount of the silicon ions, fluorine and oxygen in the system, respectively.

## RESULTS AND DISCUSSION

The  $\text{KF-KCl-K}_2\text{SiF}_6$  and  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  melts are essentially different because one of them includes an oxygen-containing  $\text{SiO}_2$  compound. Silicon dioxide is a covalently bonded compound. Thus, there are only compounds with an ionic bond type in the  $\text{KF-KCl-K}_2\text{SiF}_6$  system. The  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  system includes components with ionic and covalent bond types. In practice, in the presented systems, the different types of the electrode deposits and various types of complexes were found in an experimental investigation.<sup>9</sup>

When studying the bond energies in the complexes, the principle expressed by Eq. (1) was applied. According to Eq. (1), the bond energy is equivalent to the energy required to divide the entire system into separate parts. A compound can be stable if the total potential energy of its parts is negative. The most preferred is the state with the most negative energy.

### *The silicon complexes in $\text{KF-KCl-K}_2\text{SiF}_6$*

DFT calculations were accomplished of the bond energy for the silicon complexes of the various structures that can be formed in  $\text{KF-KCl-K}_2\text{SiF}_6$  melts. Silicon complexes of the  $[\text{SiF}_6]^{2-}$  and  $[\text{SiF}_7]^{3-}$  types were considered as the main structures. Under normal conditions, such structures can be distinguished in the  $\text{K}_2\text{SiF}_6$  and  $\text{K}_3\text{SiF}_7$  crystal lattices. These components may be present in the composition of the melts under study.

$\text{K}_2\text{SiF}_6$  is a component of the initial  $\text{KF-KCl-K}_2\text{SiF}_6$  melt, and  $\text{K}_3\text{SiF}_7$  can be formed because of interactions occurring in melts of this type. There is a crystallization field of  $\text{K}_3\text{SiF}_7$  in the  $\text{KF-KCl-K}_2\text{SiF}_6$  phase diagram.<sup>16</sup>  $\text{K}_3\text{SiF}_7$  was found in  $\text{KF-KCl-K}_2\text{SiF}_6$  melts by X-ray phase analysis.<sup>9</sup> The calculation

results of the bond energies for  $\text{Si}^{4+}$  in the silicon complexes are presented in Table I.

TABLE I. Total energies, bond energies, and lengths of fluoride complexes  $[\text{SiF}_6]^{2-}$

Species	The number of $\text{K}^{+a}$	Total energy eV	Bond energies eV	Average bond length of Si-F, Å	Average bond length of K-F, Å
$[\text{SiF}_6]^{2-}$	—	-4149.995	-113.195	1.765	—
	1	-4168.484	-122.591	1.774	2.397
	2	-4170.318	-124.852	1.727	2.434
	3	-4194.061	-129.981	1.766	2.466
$[\text{SiF}_7]^{3-}$	—	Destruction of complex into $[\text{SiF}_6]^{2-}$ and $\text{F}^-$			
	1	-4836.636	-122.915	1.770	2.321
	2	-4853.940	-131.125	1.767	2.324
	3	-4866.793	-134.885	1.711	2.287

<sup>a</sup>In the second coordination sphere

The silicon complex in the melt as a part of the second coordination sphere may contain potassium cations. The introduction of  $\text{K}^+$  into the environment of the  $[\text{SiF}_6]^{2-}$  and  $[\text{SiF}_7]^{3-}$  complexes was also investigated. The structure of the complex compounds  $[\text{SiF}_6]^{2-}$  and  $[\text{SiF}_7]^{3-}$  with the addition of two potassium cations to the second coordination sphere is shown in Fig. 1.

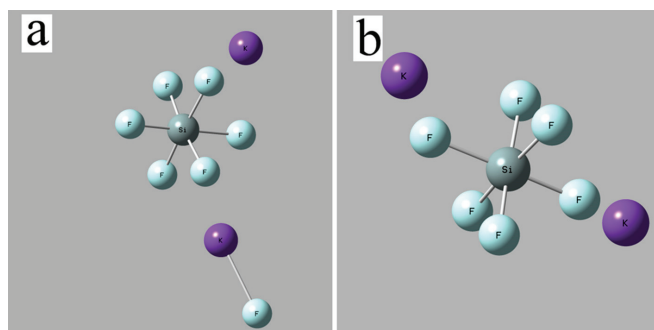


Fig. 1. Complexes  $[\text{SiF}_7]^{3-}$  (a) and  $[\text{SiF}_6]^{2-}$  (b) in the presence of two  $\text{K}^+$ .

The calculations revealed (Fig. 1a) that  $\text{K}^+$  captures the fluorine atom. The interaction of  $\text{K}^+$  with the fluorine atom leads to destruction of the  $[\text{SiF}_7]^{3-}$  complex. The destruction of the complex  $[\text{SiF}_7]^{3-}$  occurs with the formation of  $[\text{SiF}_6]^{2-}$  and  $[\text{KF}]^0$ . The addition of two potassium cations (Fig. 1b) does not cause the destruction of the  $[\text{SiF}_6]^{2-}$  structural unit. The  $[\text{SiF}_6]^{2-}$  complex remains stable with the addition of two  $\text{K}^+$ .

According to an investigation,<sup>8</sup> the considered structural units of the  $\text{KF-KCl-K}_2\text{SiF}_6$  melt can only be represented as silicon fluoride complexes. Calculation in the absence of  $\text{K}^+$  established the lengths of the Si-F bonds in the  $[\text{SiF}_7]^{3-}$  and  $[\text{SiF}_6]^{2-}$  complexes. The result obtained correlates with the data

regarding the structure of  $\text{K}_3\text{SiF}_7$ <sup>17</sup> and  $\text{K}_2\text{SiF}_6$ .<sup>18</sup> Under the same conditions, the  $[\text{SiF}_7]^{3-}$  structure has the most negative total energy. The bond energies for the  $[\text{SiF}_7]^{3-}$  and  $[\text{SiF}_6]^{2-}$  groups are comparable. However, the  $[\text{SiF}_6]^{2-}$  group with an average bond energy of  $-113.195$  eV is the most probable. The introduction of potassium cations affects the total energy of the system and the bond energy in the silicon complex groups. The bond length becomes longer in the presence of  $\text{K}^+$  in the second coordination sphere. When  $\text{K}^+$  is introduced into the second coordination sphere of  $[\text{SiF}_7]^{3-}$ , a K–F bond is formed, and the Si–F bond length increases. In all considered cases, the bond angles of F–Si–F in the  $[\text{SiF}_6]^{2-}$  and  $[\text{SiF}_7]^{3-}$  complexes are close to  $90^\circ$ .

With the addition of  $\text{K}^+$  to the  $[\text{SiF}_6]^{2-}$  complex, the bond length can either increase or decrease, and only a small change in the magnitude of the angles in the range from  $86$  to  $94^\circ$  occurs. The introduction of  $\text{K}^+$  into the environment of the  $[\text{SiF}_7]^{3-}$  complex affects the bond energy more significantly than the corresponding addition of  $\text{K}^+$  to the  $[\text{SiF}_6]^{2-}$  complex. In this case, the bond energies in  $[\text{SiF}_7]^{3-}$  become more negative than the corresponding bond energies in  $[\text{SiF}_6]^{2-}$ . For both types of complexes, when  $\text{K}^+$  is present, there is a change in the bond lengths and angles. Such a change in the bond lengths may be caused by a temperature alteration. The F–K–F bond angle is close to  $60^\circ$  with a deviation of  $\pm 2^\circ$ . However, if the potassium is added to the second coordination sphere of the  $[\text{SiF}_7]^{3-}$  complex, the compound is stabilized by the formation of F–K–F bonds, with an angle that ranges from  $130$  to  $140^\circ$ , and the K–F bond length is approximately  $2.3$  Å. The broadening of the vibrational bands for silicon complexes in the Raman spectra was associated with changes in the angles between the bonds and the lengths of the bonds.<sup>9</sup> The  $[\text{SiF}_6]^{2-}$  and  $[\text{SiF}_7]^{3-}$  complexes were tested for the thermal stability in the Nose–Hoover thermostat. The results are presented in Table II.

TABLE II. Thermal stability of the silicon fluoride complexes

Species	Temperature, K	Total energy, eV	Bond energies, eV	Average bond length Si–F, Å
$[\text{SiF}_6]^{2-}$	973	–4148.870	–112.086	1.760
	1023	–4147.864	–113.485	1.770
	1043	–4147.527	–111.058	1.811
	1073	–4148.144	–111.345	1.827
$[\text{SiF}_7]^{3-}$	973–1073	Destruction of complex at $[\text{SiF}_6]^{2-}$ and $\text{F}^-$		

The  $[\text{SiF}_6]^{2-}$  remained the only stable complex in the temperature range  $973$ – $1073$  K. A general view of the  $[\text{SiF}_6]^{2-}$  complex after  $2000$  fs at  $973$  K is given in Fig. 2.

The  $[\text{SiF}_7]^{3-}$  complex was unstable. Its destruction with the formation of  $[\text{SiF}_6]^{2-}$  and the  $\text{F}^-$  was observed. This is in a good agreement with the data in the literature,<sup>9</sup> in which bond oscillations were registered only for the  $[\text{SiF}_6]^{2-}$

groups, which was reflected in the spectra at 988 and 1043 K. Moreover, the presence of  $K_3SiF_7$  was determined only in the solid sample by means of X-ray phase analysis.<sup>9</sup> The data proves that as the temperature increases, the bond length in the  $[SiF_6]^{2-}$  complex rises, while the bond energy experiences vibrations. Checking the temperature stability did not lead to a change in bond angles.

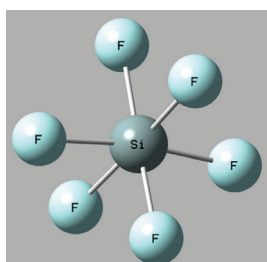


Fig. 2. Silicon complex  $[SiF_6]^{2-}$  at 973 K (2000 fs).

Thus, the obtained results indicate the stability of the  $[SiF_6]^{2-}$  complex groups in the  $KF-KCl-K_2SiF_6$  melt within the range of 973–1073 K. The study of the thermal stability allowed identification of the unstable complex  $[SiF_7]^{3-}$ . Such calculations for the structure of melts are likely to help in the prediction of the transformations of complexes in halide melts, associated with an increase in temperature.

#### *The silicon complexes in $KF-KCl-K_2SiF_6-SiO_2$*

The melts based on  $KF-KCl-K_2SiF_6-SiO_2$  contain oxyfluoride and silicate silicon complexes of different compositions. According to the results of high-temperature Raman spectroscopy,<sup>9</sup> the following silicon complexes were identified:  $[SiO_3F]^{3-}$  and  $[SiO_4]^{4-}$ . Some conclusions were made<sup>19,20</sup> regarding the presence of the  $[SiO_2F_2]^{2-}$  groups in the products of the interactions of silicon dioxide and alkali fluorides.

However, the vibrational bands for the silicon complexes of the  $[SiO_2F_2]^{2-}$  type were not registered.<sup>9</sup> The processes of the interaction between  $SiO_2$  and  $KF-KCl-K_2SiF_6$  in the molten media can be specified based on the data of quantum chemical reports. Such studies will allow conclusions related to the possibility of the existence and stability of the silicon oxide–fluoride complexes to be drawn. In this work, the results for oxyfluoride and silicate complexes of silicon are presented. The bond energies of the  $[SiO_2]$  complexes (with one terminal oxygen atom), the  $[SiO_3]^{2-}$  (with two terminal oxygen bonds), the  $[SiO_4]^{4-}$  (with four terminal oxygen atoms) allow a suggestion about the most probable complex in the  $KF-KCl-K_2SiF_6-SiO_2$  melt to be made. The calculation results of the bond energies of the silicate complex groups of silicon are presented in Fig. 3.

An increase in the oxygen content and a rise of the excess negative charge of the silicate complexes results in a decrease in the bond energy. Moreover, it was



found that the addition of  $K^+$  to the environment of the possible silicate complexes of silicon leads to an even more significant decrease in the Si–O bond energy. According to the calculations of the average bond energy of the complexes, the  $[\text{SiO}_4]^{4-}$  complex with four terminal oxygen atoms is the most probable among the silicon oxide groups embedded in the ionic melt. The bond energies were calculated for the oxyfluoride silicon complexes  $[\text{SiO}_3\text{F}]^{3-}$ ,  $[\text{SiO}_2\text{F}_2]^{2-}$  and  $[\text{SiOF}_3]^-$ . The complexes composition has effects on the energy characteristics and the Si–F bond length was determined for the oxyfluoride complexes in comparison with the corresponding data for  $[\text{SiO}_4]^{4-}$ . The results are listed in Tables III and IV.

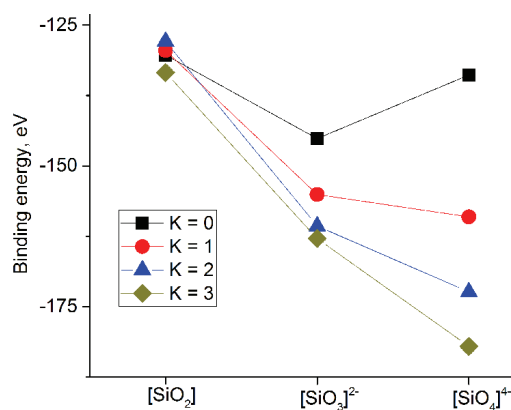


Fig. 3. Calculations of the bond energy in the oxide complexes of silicon  $[\text{SiO}_2]$ ,  $[\text{SiO}_3]^{2-}$  and  $[\text{SiO}_4]^{4-}$ .

According to the simulation, the total energies of silicon fluoride and silicate complexes ( $[\text{SiO}_3\text{F}]^{3-}$ ,  $[\text{SiO}_2\text{F}_2]^{2-}$ ,  $[\text{SiOF}_3]^-$  and  $[\text{SiO}_4]^{4-}$ ) have negative values comparable in magnitude. The presence of fluorine in the silicon complexes leads to a change in the bond energy. In the absence of  $K^+$  in the neighborhood of the complexes, the transition from  $[\text{SiO}_4]^{4-}$  to  $[\text{SiO}_3\text{F}]^{3-}$  results in a decrease in the bond energy of the silicon complex and the appearance of a more compact package with a shorter bond length.

A further increase of the fluorine content in the complexes leads to a bond energy rise. The minimum of the bond energy characterizes  $[\text{SiO}_3\text{F}]^{3-}$  as the most stable complex, since oxide–fluoride group has stronger bonds. Thus, the conversion of the  $[\text{SiO}_4]^{4-}$  to  $[\text{SiO}_3\text{F}]^{3-}$  becomes possible, which was confirmed by the high-temperature Raman spectra.

The length of potassium bonds is in the range from 2.4 to 2.6 Å and does not depend on the number of potassium in the second coordination sphere of the complex compound. Complex compounds that do not contain potassium in the second coordination sphere are symmetric because compound  $[\text{SiO}_4]^{4-}$  has six approximately equal bond angles equal to  $109.5^\circ$ , while the addition of potassium leads to a change in bond angles in the complex compound. For example, in the



same compound  $[\text{SiO}_4]^{4-}$  one angle decreased to  $104.7^\circ$ , two angles remained in the region of  $109^\circ$  and three angles increased to  $110\text{--}111^\circ$ .

TABLE III. Total energies, and bond energies and lengths of fluoride, oxyfluoride, and oxygen complexes of silicon

Species	The number of K <sup>+</sup> <sup>a</sup>	Total energy, eV	Bond energies, eV	Bond length of Si-F, Å	Bond length of Si-O, Å
$[\text{SiO}_4]^{4-}$	–	–1837.328	–133.840	–	1.743
	1	–1871.646	–159.064	–	1.690
	2	–1894.075	–172.400	–	1.695
	3	–1912.837	–182.068	–	1.707
$[\text{SiO}_3\text{F}]^{3-}$	–	–2090.455	–137.553	1.680	1.567
	1	–2115.860	–183.692	1.754	1.666
	2	–2135.396	–164.307	forms K-F	1.620
	3	–2149.738	–169.556	1.946	1.653
$[\text{SiO}_2\text{F}_2]^{2-}$	–	–2337.260	–134.944	1.775	1.610
	1	–2355.875	–144.466	1.770	1.620
	2	–2334.200	–113.698	1.736	1.573
	3	[SiO <sub>2</sub> F] <sup>–</sup> and [KF] <sup>0</sup> complex formation			
$[\text{SiOF}_3]^-$	–	–2577.480	–125.752	1.939	1.664
	1	–2591.096	–130.273	1.674	1.585
	2	–2601.174	–131.258	1.698	1.572
	3	–2608.313	–129.304	1.687	1.567

<sup>a</sup>In the second coordination sphere

TABLE IV. Bond angles and lengths of fluoride, oxyfluoride and oxygen complexes of silicon

Species	The number of K <sup>+</sup> <sup>a</sup>	F–Si–F bond angle range, °	F–Si–O bond angle range, °	O–Si–O bond angle range, °	Bond length of	
					K–F, Å	K–O, Å
$[\text{SiO}_4]^{4-}$	–	–	–	109.5	–	–
	1	–	–	104.7–111.2	–	2.623
	2	–	–	108.3–111.6	–	2.530
	3	–	–	98.1–114.8	–	2.542
$[\text{SiO}_3\text{F}]^{3-}$	–	–	101.1	116.62	–	–
	1	–	105.2	109–115.54	–	2.547
	2	–	–	115.6–126.4	2.410	2.652
	3	–	92.84–104.43	118.36	2.561	2.538
$[\text{SiO}_2\text{F}_2]^{2-}$	–	94.58	107.22	128.25	–	–
	1	92.67	109.72	126.91	2.411	2.445
	2	83.39	94.77	133.50	2.475	2.464
	3	[SiO <sub>2</sub> F] <sup>–</sup> and [KF] <sup>0</sup> complex formation				–
$[\text{SiOF}_3]^-$	–	99.22	118.13	–	–	–
	1	100.15	108.41–121.8	–	2.586	2.526
	2	93.3–101.77	117.25	–	2.517	2.426
	3	94.7–102.69	116.34–121.1	–	2.546	2.460

<sup>a</sup>In the second coordination sphere

The structures of the complex compounds  $[\text{SiO}_4]^{4-}$ ,  $[\text{SiO}_3\text{F}]^{3-}$ ,  $[\text{SiO}_2\text{F}_2]^{2-}$  and  $[\text{SiOF}_3]^-$  when adding three potassium cations are shown in Fig. 4.

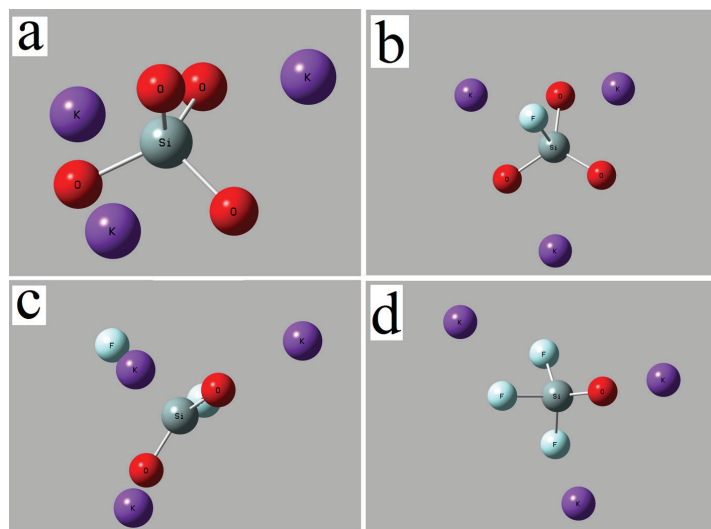


Fig. 4. Geometric structure of silicon complexes: a)  $[\text{SiO}_4]^{4-}$ , b)  $[\text{SiO}_3\text{F}]^{3-}$ , c)  $[\text{SiO}_2\text{F}_2]^{2-}$  and d)  $[\text{SiOF}_3]^-$  with the addition of three potassium cations to the second coordination sphere.

The results of the structure calculation reveal (Fig. 4c) that the addition of potassium ions leads to the destruction of  $[\text{SiO}_2\text{F}_2]^{2-}$  and the formation of the  $[\text{SiO}_2\text{F}]^-$  and  $[\text{KF}]^0$  complexes. In the cases of  $[\text{SiO}_4]^{4-}$ ,  $[\text{SiO}_3\text{F}]^{3-}$  and  $[\text{SiOF}_3]^-$  (Fig. 4a, b and d respectively), hardening of the compound occurs (data in Table III).

The addition of  $\text{K}^+$  to the environment of the considered complexes (Table III), as a rule, leads to a decrease in the total energy. Simultaneously, the nature of the change in the bond length is debatable. The appearance of a potassium cation in the neighborhood of a  $[\text{SiO}_4]^{4-}$  complex creates a decrease in the Si–O bond length. With the addition of the next  $\text{K}^+$ , the Si–O bond length no longer decreases. The presence of  $\text{K}^+$  near an  $[\text{SiO}_3\text{F}]^{3-}$  complex leads to an increase in the length of the Si–F and Si–O bonds. However, with further addition of  $\text{K}^+$ , a consistent increase in the length of these bonds was not observed. In the  $[\text{SiO}_2\text{F}_2]^{2-}$  system, with the addition of  $\text{K}^+$ , a wave-like change in the length of the Si–O and Si–F bonds occurs. The addition of  $\text{K}^+$  to the  $[\text{SiOF}_3]^-$  system leads to a consistent decrease in the length of the Si–F and Si–O bonds.

Thus, calculations revealed that the most probable silicon complexes are  $[\text{SiO}_3\text{F}]^{3-}$  and  $[\text{SiO}_4]^{4-}$ . The thermal stability was investigated precisely for these complexes. The results are presented in Table V.

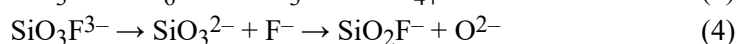
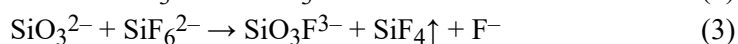
The  $[\text{SiO}_3\text{F}]^{3-}$  complex groups demonstrate a thermal stability at temperatures below 1043 K. There are the conditions for the transformation of  $[\text{SiO}_4]^{4-}$

to  $[\text{SiO}_3\text{F}]^{3-}$  in the temperature range under study. However, due to the similar values of the bond energy, this transformation is likely to be retarded. Such a chemical reaction was reported<sup>21</sup> during the cathode process when studying the mechanism of the silicon electroreduction in  $\text{KF-KCl-K}_2\text{SiF}_6$  melts, which was assigned to  $\text{SiO}_2$  dissolution.

TABLE V. The results of studying the thermal stability of the complexes  $[\text{SiO}_3\text{F}]^{3-}$  and  $[\text{SiO}_4]^{4-}$

Species	Temperature, K	Total energy, eV	Bond energies, eV	Average bond length of Si-F, Å	Average bond length of Si-O, Å
$[\text{SiO}_3\text{F}]^{3-}$	973	-2088.946	-139.169	2.1984	1.670
	1023	-2089.249	-139.467	1.886	1.617
	1043	Segregates into $\text{SiO}_3^{2-}$ and $\text{F}^-$			
	1073				
$[\text{SiO}_4]^{4-}$	973	-1836.157	-136.832	—	1.763
	1023	-1836.254	-136.926		1.750
	1043	-1835.846	-137.105		1.781
	1073	-1835.966	-136.671		1.761

Temperature increases above 1043 K resulted in the destruction of the  $[\text{SiO}_3\text{F}]^{3-}$  complex with the formation of  $[\text{SiO}_3]^{2-}$  and  $\text{F}^-$ . The conditions when  $[\text{SiO}_4]^{4-}$  becomes the most possible are created at temperatures of 1043 K and 1073 K. Presumably, under these conditions, decomposition of the  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  melt can proceed due to the conversion of the oxyfluoride complexes to the silicate one:



In general, this was confirmed by DSC data of the  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  melt presented in the literature.<sup>9</sup> It was found that intensive  $\text{SiF}_4$  gas evaporation from the melt began, accompanied by a mass loss, after reaching 1033 K. The research results revealed that in the molten  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  system the complexes  $[\text{SiF}_6]^{2-}$ ,  $[\text{SiO}_4]^{4-}$  and  $[\text{SiO}_3\text{F}]^{3-}$  can be considered relatively stable in the temperature range 973–1023 K. The most probable group for  $\text{KF-KCl-K}_2\text{SiF}_6$  melts is  $[\text{SiF}_6]^{2-}$  in the temperature range 973–1073 K. The stable silicon complexes for the  $\text{KF-KCl-K}_2\text{SiF}_6$  and  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  melts are presented in Fig. 5.

It was demonstrated that the oxide complexes  $[\text{SiO}_4]^{4-}$  and  $[\text{SiF}_6]^{2-}$  are approximately comparable in size. However, the  $[\text{SiO}_3\text{F}]^{3-}$  oxide-fluoride complex of silicon is larger than  $[\text{SiF}_6]^{2-}$ . Consequently, an increase in the complexes size should be expressed in a rise of diffusion difficulties. An increase in the

diffusion difficulties with the appearance of oxygen in the  $\text{KF-KCl-K}_2\text{SiF}_6$  melt was reported in the literature.<sup>20</sup> In general, the obtained data are in a good agreement with results in the literature<sup>9</sup> and supplement them in terms of the cause of the thermal instability of  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  melts at temperature above 1033 K.

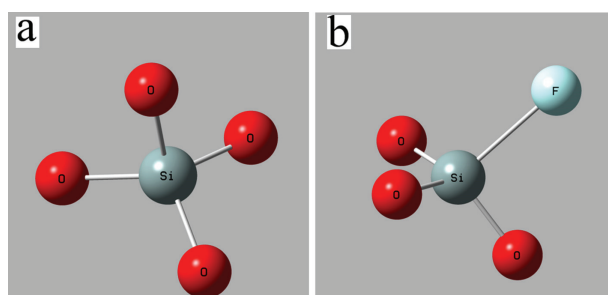


Fig. 5. Complex compounds  $\text{SiO}_4^{4-}$  and  $\text{SiO}_3\text{F}$  at 973 K.

#### CONCLUSIONS

The structures of complexes in the  $\text{KF-KCl-K}_2\text{SiF}_6$  and  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  systems was studied using DFT calculations; an effect of temperature change on the stability of the silicon complexes was found. The bond energies of the silicon complexes were calculated and their structure was considered. It was established that the appearance of fluorine in the composition of silicon oxide complexes leads to a decrease in the bond energy. Increasing the fluorine content in the series  $[\text{SiO}_3\text{F}]^{3-} \rightarrow [\text{SiO}_2\text{F}_2]^{2-} \rightarrow [\text{SiOF}_3]^-$  leads to a rise in the bond energy. The effect of the introduction of potassium ions into the second coordination sphere of the silicon complexes was discussed. The introduction of excess  $\text{K}^+$  into the environment of the complexes changes the bond energy. In the case of  $[\text{SiO}_3\text{F}]^{3-}$ , excess  $\text{K}^+$  leads to the destruction the complex. It was found that in the presence of  $\text{K}^+$  in the environment of  $[\text{SiO}_3\text{F}]^{3-}$  complexes, an increase in the Si-F bond length occurs. The addition of  $\text{K}^+$  to the environment of  $[\text{SiOF}_3]^-$  and  $[\text{SiO}_4]^{4-}$  complexes leads to a decrease in the length of the Si-F and Si-O bonds. In the  $[\text{SiO}_2\text{F}_2]^{2-}$  system, with the addition of  $\text{K}^+$ , minimal changes in the lengths of the Si-O and Si-F bonds were observed.

It was determined that the most stable complex groups in the  $\text{KF-KCl-K}_2\text{SiF}_6$  melt are silicon fluoride complexes of the  $[\text{SiF}_6]^{2-}$  type. It was proved that the  $[\text{SiF}_6]^{2-}$  complexes were thermally stable in the range of 973–1073 K. It was also revealed that the  $[\text{SiF}_6]^{2-}$ ,  $[\text{SiO}_4]^{4-}$  and  $[\text{SiO}_3\text{F}]^{3-}$  complexes can be typical for  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  melts. The study of the thermal stability indicated that the most probable is the  $[\text{SiO}_3\text{F}]^{3-}$  complex at temperatures below 1043 K. At temperature as high as 1043 K,  $[\text{SiO}_3\text{F}]^{3-}$  was destroyed and

$[\text{SiO}_4]^{4-}$  became the most probable complex of silicon. The process of converting  $[\text{SiO}_3\text{F}]^{3-}$  to  $[\text{SiO}_4]^{4-}$  is accompanied by a mass loss of the melt.

The obtained data of DFT calculations are in a good agreement with the experimental study of the  $\text{KF-KCl-K}_2\text{SiF}_6$  and  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  melts. Such a calculation method in addition to experiment can be used to estimate the stability of the structural units of a melt. The basis for the modeling can be the data related to the structure of both solid and liquid samples. The understanding of the temperature effect on the stability of the structures allows the transformations associated with the reconstruction of the complexes to be taken into account.

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## ИЗВОД

НА DFT ЗАСНОВАНА ИЗРАЧУНАВАЊА СТРУКТУРА СИЛИЦИЈУМОВОГ КОМПЛЕКСА  
У  $\text{KF-KCl-K}_2\text{SiF}_6$  И  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  РАСТОПИМА

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Дужина и енергија веза у комплексним анјонима силицијума, формираним у  $\text{KF-KCl-K}_2\text{SiF}_6$  и  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  растопима, процењене су користећи прве принципе молекулске динамике, помоћу програма Siesta. Проучен је утицај  $\text{K}^+$  (из друге координационе сфере) на стабилност ових комплекса. Нађено је да се дужина веза у комплексима силицијума мења са порастом количине калијумових јона. Утврђено је да су следећи комплекси  $[\text{SiO}_4]^{4-}$ ,  $[\text{SiO}_3\text{F}]^{3-}$ ,  $[\text{SiF}_6]^{2-}$  најстабилнији у  $\text{KF-KCl-K}_2\text{SiF}_6$  и  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  растопима.  $[\text{SiO}_4]^{4-}$  и  $[\text{SiF}_6]^{2-}$  су термички стабилни у растопима соли у температурском опсегу од 923–1073 K, док је  $[\text{SiF}_7]^{3-}$  структура, која је типична за решетку кристалног  $\text{K}_3\text{SiF}_7$ , нестабилна у овом температурском опсегу. У растопима  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$ , створени су услови изнад 1043 K који дозвољавају трансформацију  $[\text{SiO}_3\text{F}]^{3-}$  у  $[\text{SiO}_4]^{4-}$ . На проучаваним температурама, дужина Si-F везе је у распону од 1,5–1,9 Å, а дужина Si-O везе је 1,5–1,7 Å. Добијени резултати се добро слажу са *in situ* подацима Раманске спектроскопије за  $\text{KF-KCl-K}_2\text{SiF}_6$  и  $\text{KF-KCl-K}_2\text{SiF}_6\text{-SiO}_2$  растопе.

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